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EFFECT OF CATHODE MATERIALS ON THE ELECTROCHEMICAL REDUCTION OF L-CYSTINE TO L-CYSTEINE

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Industrial production of L-cysteine is based on the electro- redution of L-cystine in acidic electrolytes using either lead or silver cathodes. When lead is used as the cathode material the current efficiency is more than 85 %. But the product is found to be contaminated with lead. When silver is used as the cathode material the product is free from heavy metals but the current efficiency falls sharply to 50-55%. To perform the electrolysis with high current efficiency and prevent the heavy metal contamination in the product, different cathode materials like lead-silver alloy, lead-tin alloy, copper, zinc deposited copper, graphite and tin deposited copper were used for the reduction and the results obtained in the laboratory scale studies are presented in this paper. The effect of current density, electrolysis temperature, depolariser concentration on current efficiency, yield efficiency and purity of the product are discussed.

Keywords: L-cysteine, heavy metal contamination, depolariser.

INTRODUCTION

The world wide practiced industrial route to L-cysteine is by the electrochemical reduction of L-cystine, usually in acid solution. The estimated world market for L-cysteine is approximately 1000- 1500 tonnes per annum [1] with the high value product commanding prices $ 60-100/Kg. In common with almost all amino acids, there is no demand for the D-isomer or the racemic mixture owing to their lack of function in biological systems. The major application areas are in food-stuffs, cosmetics and pharmaceutical industries.

Pharmaceutical industries require L-cysteine to produce N-acetyl- L-cysteine, S-carboxymethyl-L-cysteine and L-cysteine methyl ester, which are used as mucolytic agents in the treatment of bronchitis and nasal catarrh. Many other derivatives are employed in the treatment of hepatitis, respiratory disorders, dermatitis and radiation damage. L-cysteine is itself required as an antidote to snake venom [2,3].

Number of alternative routes are reported to L-cysteine in addition to the electrochemical reduction of L-cystine, but none of them can compete with the electrochemical method. Enzymatic methods have recently been reported to be developed in the laboratory [4]; but it has yet to be proved in industrial scale. Many chemical routes are also available [6-8]. However, all the chemical methods are expensive, multi-step process which produces a racemic mixture that must be optically resolved to give the desired L-isomer and the D-isomer for racemization and recycling. The additional process represents a significant economic disincentive. Considering the defects existing in the biochemical and chemical methods the major world producers like Degussa, Diamalt, Ajinomotto, etc. are manufacturing L-cysteine employing only electrochemical method. Even though many electrode materials have been studied in laboratory scale some manufactures are employing lead cathodes, in which lead was found to be present in the product; in such cases the products can be used for external applications only. Others are using silver electrodes as working electrodes; in this case the product is free from any heavy metal contamination. But the current efficiency is found to be only 40-50%, which results in higher energy consumption. To develop an electrochemical method where the metal ion pick up can be avoided/minimised as well as the energy consumption can be brought down, experiments were carried out with different cathode materials and the results are presented in this paper.

EXPERIMENTAL

All chemicals used in this studies are LR grade only; L-cystine (IP) was supplied by M/S Protchem India Limited, Madras. Two compartment PVC box, having Nafion 326 as separator was used as the cell. Catholyte was stirred during the electrolysis using a magnetic stirrer. Ablab constant current generator was used as the power source. Noble metal oxide coated titanium electrode was used as the counter electrode in all the experiments. 30 gms. of L-cystine was dissolved in 1:1 aqoues hydrochloric acid and heated to 343-348 K; 0.25 gms. activated charcoal was added to the hot solution of L-cystine and the solution temperature was maintained at 338-348K with constant stirring. Then the solution was filtered using Whatman filter paper No 3 after cooling it to room temperature. The filtered solution was used as the catholyte and electrolysis was performed. After passing the theoretical current the catholyte was tested for L-cystine, periodically and the electrolysis was continued till all the L-cystine in the catholyte is converted. The electrolyte after electrolysis was once again heated to 343 K; charcoal treatment was given to improve the quality of the product. The product was recovered from the purified electrolyte by vacuum concentration.

RESULTS AND DISCUSSION

Experiments were carried out using lead, lead-silver alloy, lead-tin alloy, copper, tin deposited copper, zinc deposited copper and graphite as the working electrode. Effect of current density, depolariser concentration and temperature on current efficiency and metal ion pick up during the electrolysis were studied separately for each electrode. Even though the cell is operated at constant current density the increase of the depolariser concentration results in the increase in the metal ion pick up. Similarly, when the depolariser concentration is maintained at a particular concentration, the increase in the cathode current density results in the decrease of the metal ion pick up during the electrolysis. Electrolyte temperature, when increased, the metal ion pick up also increases.

Table I shows the results obtained with different cathode material at their optimum condition of electrolysis. When lead is used as the working electrode, the metal ion pick up is very high even though the cell is operated at very high current density, nearly 30 A/dm^2 in stage 1 (till the hydrogen evolution was observed at 30 A/dm^2) and 20 A/dm^2 in stage 2 (till the hydrogen evolution takes place after reducing the current density to 20 A/dm^2). When the

TABLE I: Results obtained while using different cathode materials

Anolyte	:	Aqueous hydrochloric acid (1:1) 100 ml
Catholyte	:	Aqueous hydrochloric acid (1:1) 90 ml
Anode	:	Dimensionally stable noble metal oxide coated titanium 2.0 cm x 5.5 cm (0.11 dm^2)
Cathode area	:	0.11 dm^2
Separator	:	Nafion 326
Depolariser added	:	30 g
Temperature	:	309-318 K
Cell voltage	:	3.8-4.3 V

Cathode	Lead	Lead*	Sn/Cu (thin)	Sn/Cu (thick)	Zn/Cu	Copper	Pb-Sn alloy	Graphite	Pb-Ag alloy
Cd (A/dm^2) (Stage I)	30.00	30.00	12.00	12.00	12.00	12.00	36.000	13.00	16.00
Current passed (A) (Stage I)	4.50	4.40	6.25	6.00	5.25	6.00	6.825	6.00	6.00
Cd (A/dm^2) (Stage II)	20.00	20.00	6.00	6.00	6.00	6.00	18.000	6.80	8.00
Current passed(A) (Stage II)	2.00	2.00	1.50	1.50	3.00	3.00	3.000	2.00	2.75
Cd (A/dm^2) (Stage III)	10.00	10.00	4.00	4.00	-----	-----	-----	-----	-----
Current passed(A)(Stage III)	0.50	0.50	1.50	1.50	-----	-----	-----	-----	-----
Total current (A)	6.87	6.87	9.25	8.50	8.25	9.00	9.825	8.00	8.75
Excess current passed (%)	2.00	2.00	38.00	27.00	23.00	34.00	46.000	19.00	30.00
Product formed (g)	33.70	32.66	46.36	43.38	38.63	39.34	34.770	40.57	41.09
Metal ion content (ppm)	120.00	84.00	21.00	30.00	15.00	16.00	8.000	-----	10.00

* The depolariser was added in two equal instalments

depolariser addition to the catholyte was in two equal installments i.e. the addition of the second installment after observing hydrogen evolution at the cathode compartment, the metallic contamination in the product becomes less. In the case of tin deposited copper electrode the product yield was very high, almost quantitative; the metallic impurity is relatively low. The metallic impurity becomes still less when the tin deposit on the copper cathode is very thin. The product yield and the metallic impurity were less, in the case of zinc deposited cathodes. When alloy electrodes like lead-tin and lead-silver are used as the cathode material the product yield is very high; and the quality of the product was also good, due to the low metal ion pick up during the electrolysis. The cell can be operated at very high current density range 30-38 A/dm^2. When the graphite electrode is used as the cathode material the current efficiency, yield efficiency and quality of the product were excellent; but the cell can be operated only at normal current densities like 10-16 A/dm^2.

CONCLUSION

Out of the different electrodes used as the working electrode, alloy electrodes and graphite electrode are giving better results in terms of current efficiency, yield efficiency and quality of the product. The current density recommended for Pb-Sn alloy electrodes around 30-35 A/dm^2 and for the graphite electrode the current density range, found suitable is 12-16 A/dm^2. When Pb-Ag alloy electrode is used the current density range found viable is 15-18 A/dm^2.

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